

Summary of Research Reports for NAG1-2191 and NAG1-02083

Modeling of Isotope Fractionation in Stratospheric CO₂, N₂O, CH₄, and O₃: Investigations of Stratospheric Chemistry and Transport, Stratosphere-Troposphere Exchange, and Their Influence on Global Isotope Budgets

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Research Objectives

Until recently, the stable isotopic composition of chemically and radiatively important stratospheric species, such as ozone (O₃), carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄), was largely unexplored, despite indications from the few measurements available and theoretical studies that global-scale isotopic variations will provide a unique tool for quantifying rates of global-scale mass transport into, within, and out of the stratosphere and for understanding the mechanisms of chemical reactions involved in ozone production. The number and geographical extent of observations are beginning to increase rapidly, however, as access to the stratosphere, both directly and by remote-sensing, has increased over the last 10 years and as new analytical techniques have been developed that make global-scale isotope measurements by whole-air sampling more feasible. The objective of this study, begun in April 1999, is to incorporate into the Livermore 2D model the likely photochemical fractionation processes that determine the isotopic compositions of stratospheric CO₂, N₂O, CH₄, and O₃, and to use the model results and new observations from NASA field campaigns in 1996 and 1997 to investigate stratospheric chemistry and mass transport. Additionally, since isotopic signatures from the stratosphere are transferred to the troposphere by downward transport at middle and high latitudes, the isotopic compositions may also serve as sensitive tracers of stratosphere-to-troposphere transport. Comparisons of model results with stratospheric and upper tropospheric observations from these campaigns, as well as with ground-based observations from new NOAA and NSF-sponsored studies, will help determine whether the magnitudes of the stratospheric fractionation processes are large enough to use as global-scale tracers of transport into the troposphere and, if so, will be used to help constrain the degree of coupling between the

troposphere and the stratosphere. Moreover, while isotopic studies in the troposphere have already provided a wealth of information on the natural and anthropogenic sources and sinks of CO_2 , CH_4 , and N_2O , the influence of stratospheric fractionation processes on the tropospheric isotopic compositions has received only scant attention, despite evidence that it may be quantitatively important. The ability to model global-scale variations in the isotopic compositions of stratospheric species and their transfer to the troposphere will help distinguish between fractionation occurring in the atmosphere and that which results from biological or industrial processes, in principle allowing more accurate global budgets for CO_2 , N_2O , and CH_4 to be derived if the influence of the stratosphere is determined to be significant.

Results

In short, one of the most important findings in the work funded under these two grants is that isotopic fractionation in the stratosphere influences isotopic compositions measured at the surface to a larger degree than previously expected. For the gases CH_4 and H_2 , for example, the effect of transport and mixing of heavy isotopologues from the stratosphere is as large as their measured interhemispheric gradients at the surface, an important conclusion since the observed interhemispheric gradients serve as one of the primary constraints on biogeochemical inverse models used to deduce the magnitudes and locations of the sources and sinks of these gases in the atmosphere.

In more detail, we investigated the isotopic fractionation of CH_4 and hydrogen (H_2) in the stratosphere by incorporating isotope-specific rate coefficients into the Lawrence Livermore National Laboratory (LLNL) 2D model and comparing the model results with new observations from the NASA ER-2 aircraft (funded through a separate task under the Upper Atmosphere Research Program). The model results reveal that fractionation which occurs in the stratosphere has a significant influence on isotope compositions in the free troposphere [e.g., *McCarthy et al., 2001*], an important point which had previously been ignored, unrecognized or unquantified for many long-lived trace gases, including CH_4 and H_2 which we have focused our efforts on to date. Our analyses of the model results and new isotope observations have also been used to test how well the kinetic isotope effects are known, at least to within the uncertainties in model chemistry and transport [e.g., *McCarthy et al., 2003*]. Overall, these results represent an important step forward in our understanding of isotope fractionation in the atmosphere and demonstrate that stratospheric isotope fractionation cannot be ignored in modeling studies which use isotope observations in the troposphere to infer the global budgets of CH_4 (an important greenhouse gas) and of H_2 (a gas whose atmospheric budget must be better quantified, particularly before a large human perturbation from fuel cell use is realized). Our analyses of model results and observations from the NASA ER-2 aircraft are briefly summarized separately below for CH_4 , H_2 , and H_2O and for the contribution of these modeling studies to date to our understanding of isotope fractionation for N_2O , CO_2 , and O_3 as well.

- For the CH_4 modeling studies, kinetic isotope effects (KIEs) for its oxidation by OH, Cl, and $\text{O}(^1\text{D})$ were incorporated into the LLNL 2D model to examine how sensitive the carbon isotopic composition of CH_4 in the free troposphere is to three influences: realistic stratospheric chemistry and transport, tropospheric Cl chemistry, and use of new, experimentally-determined KIEs for the OH and $\text{O}(^1\text{D})$ sinks. At steady-state, our results

indicate that stratospheric chemistry and transport enrich tropospheric methane in ^{13}C by 0.5 to 0.6‰ (where 1‰=0.1%), tropospheric Cl chemistry as modeled enriches CH_4 by $\sim 0.3\%$, and the new KIE for the OH sink depletes modeled global methane by $>1\%$. Ignoring the stratosphere (and Cl chemistry in general) in models therefore happens to partially compensate for use of the previously accepted KIE for OH when comparisons with observations of the carbon isotopic composition of CH_4 in the free troposphere are made. In contrast, including only one of these influences increases the error relative to including none. Thus, all 3 effects are of sufficient magnitude to warrant their inclusion in inverse models in order to reduce uncertainties in the CH_4 budget. These results appear in *McCarthy et al. [2001]*. In *Rice et al. [2003]* and *McCarthy et al. [2003]*, we analyzed model results for both the carbon and hydrogen isotopic compositions of stratospheric CH_4 and compared them with new ER-2 observations in order to assess the uncertainties in our knowledge of the magnitudes of the kinetic isotope effects (KIEs) for the oxidation of CH_4 . Several of the uncertain KIEs are particularly important for deriving estimates of magnitudes of CH_4 sources to the atmosphere through inverse modeling. We also discussed how comparing the LLNL 2D model results with the new ER-2 observations and with results from other models may be used as a new diagnostic for integrated chemistry and transport in the stratosphere. In short, while absolute agreement between model results and stratospheric isotope observations for CH_4 will require additional laboratory measurements of the KIEs themselves, the relative agreement between model results for different models using the same set of KIEs can be used to reveal important differences in integrated Cl, OH, and $\text{O}(^1\text{D})$ abundances and in transport characteristics between the models. Moreover, these studies of isotope effects in methane oxidation have led my students and I to pursue new research directions that include using the ^{13}C isotopic composition of one of its byproducts, CO, as a new tracer of integrated Cl levels over the course of polar winters. Cl levels vary greatly in the Arctic vortex, both spatially and temporally, resulting in large interannual variations in Arctic ozone depletion. However, at present, large scale, time-integrated observational probes (as we propose ^{13}CO may be) are lacking. These latter results have been written up in the **doctoral dissertation of M. McCarthy** and are expected to be published within the next year.

- If society moves to a hydrogen fuel cell-based economy to mitigate the effects of greenhouse gas emissions, it is imperative that we understand the current budget of H_2 in today's atmosphere. However, the global budget for H_2 is highly uncertain, and isotope observations in the troposphere are currently serving as an added constraint. However, the isotope fractionation that occurs as CH_4 is oxidized to H_2 has not been quantified, which represents a significant uncertainty in the global H_2 isotope budget. New measurements of $\delta\text{D-H}_2$ with colleagues at Caltech and our joint analysis of the photochemical evolution of H_2 in the stratosphere resulted in publication of the first high-precision measurements of H_2 in Earth's stratosphere and their use in resolving large discrepancies in the understanding of the H_2 concentration and isotope records, thereby significantly reducing uncertainties in its current sources and sinks to the atmosphere [*Rahn et al., Nature, 2003*]. In current work following on work completed for these grants, we are performing more sophisticated isotope modeling for tropospheric and stratospheric H_2 . These latter results have been written up in the **doctoral dissertation of M. McCarthy** and are expected to be published within the next year.

- In *McCarthy et al.* [2004], we combined the new H_2 and CH_4 hydrogen isotope measurements noted above in order to infer a highly precise and accurate value for the annual mean hydrogen isotopic composition of water vapor entering the Earth's stratosphere, a key new observable that will shed light on the mechanisms of transport of air into the stratosphere and how these may change as humans alter the climate.
- The studies completed above for the isotope fractionation of CH_4 and H_2 are serving as the basis for understanding the influence of the interaction of both chemistry and transport on the isotope compositions of long-lived trace gases such as N_2O and CO_2 (for which isotope measurements have been or are currently being made on the same air samples for which CH_4 and H_2 were measured) and for O_3 . Understanding isotope fractionation for N_2O and CO_2 in the stratosphere, and the transport of the stratospheric signature to the free troposphere, is also important in understanding the global budgets of these greenhouse gases. Several papers (not cited below) for these additional trace gases which use insight from the LLNL 2D modeling for CH_4 and H_2 have been published. In addition, isotope modeling for CO_2 is currently being investigated in follow-on work to this grant.

In summary, research under these grants has now quantitatively demonstrated that (a) stratospheric photochemistry, which alters the isotopic compositions of the long-lived gases CH_4 , N_2O , CO_2 , H_2 , and H_2O in chemically interesting ways, cannot be ignored in the global isotope budgets of these species, which have been studied in the past primarily at Earth's surface.

Publications acknowledging support from these grants

(Note: underlined names are PhD students supported by these grants)

- M.C. McCarthy, K.A. Boering, T. Rahn, J.M. Eiler, A. L. Rice, S. C. Tyler, S. Schauffler, E. Atlas, and D.G. Johnson, "The hydrogen isotopic composition of water vapor entering the stratosphere inferred from high precision measurements of $\delta\text{D-CH}_4$ and $\delta\text{D-H}_2$," *J. Geophys. Res. (Atmospheres)* 109, D07304, doi:10.1029/2003JD00403, 2004.
- M.C. McCarthy, "Measurements and Modeling of the Stable Isotopic Compositions of Trace Stratospheric Gases," *PhD Dissertation*, University of California at Berkeley, December 2003.
- T. Rahn, J.M. Eiler, K.A. Boering, P.O. Wennberg, M.C. McCarthy, S. Tyler, S. Schauffler, S. Donnelly, and E. Atlas, "Extreme deuterium enrichment in stratospheric hydrogen and the global atmospheric budget of H_2 ," *Nature* 424, 918-921, 2003.
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